

The low-frequency response in the surface superconducting state of ZrB_{12} single crystal

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The large nonlinear response of a single crystal ZrB_{12} to an ac field (frequency 40 - 2500 Hz) for $H_0 > H_{c2}$ has been observed. Direct measurements of the ac wave form and the exact numerical solution of the Ginzburg-Landau equations, as well as phenomenological relaxation equation, permit the study of the surface superconducting states dynamics. It is shown, that the low frequency response is defined by transitions between the metastable superconducting states under the action of an ac field. The relaxation rate which determines such transitions dynamics, is found.

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I. INTRODUCTION

Recently high-quality superconducting ZrB_{12} single crystals with transition temperatures $T_c = 6.06$ K have been grown. The investigation of their physical properties, including electron transport, tunnel characteristics, and critical fields, have shown that the Ginzburg-Landau parameter κ is only slightly larger than the boundary between the type-I - type-II superconductor value [1, 2]. In this paper we concern the low-frequency response of a ZrB_{12} crystal when the dc external magnetic field $H_0 > H_{c2}$ is parallel to the sample surface. In spite of the fact that the sample is in the surface superconducting state (SSS) [3], no static magnetic moment is observed, while the ac response in this regime is large and nonlinear even for an ac amplitude $h_0 \ll H_0$. Indeed, at equilibrium the total surface current equals zero in SSS, the internal dc magnetic field in the bulk equals H_0 , and the magnetic moment of the specimen is small. On the other hand, the ac magnetic field drives the sample into a metastable SSS where the total surface current reaches a finite value. The internal magnetic field deviates from the external one, and as a result the ac response becomes large. The low-frequency response of superconductors in SSS was the focus of intensive experimental investigations [4, 5, 6] since the first prediction of the existence of SSS in [3]. The observed [4] wave form of the ac response, corresponding to the flux passing through the specimen, explicitly invoked a model similar to the Bean model [7]. Recently SSS attracted renewed interest from various directions as described in Ref. [8, 9, 10, 11, 12, 13]. Paramagnetic effect in a superconducting disk [8], stochastic resonance [9], the percolation transition in the field $H_0 = 0.81H_{c3}$ [10] have been observed. It was proposed to use low-frequency response for testing the quality of superconducting resonators in accelerators [11]. Surface states were observed also in single crystals of MgB_2 [12]. Our experimental results presented here show that in ZrB_{12} single crystal,

the Bean critical model of surface sheath does not give an adequate description of the observed wave form which corresponds to the flux passing through the sample. In the framework of Ginzburg-Landau theory we calculated the surface current in metastable SSS's which exists under an ac magnetic field. Observing the wave forms, we studied the metastable SSS dynamics and determined the relaxation rate under an ac field. We found that the relaxation time for transition to the equilibrium state is not constant and depends on the surplus of the free energy. This relaxation time is decreased with the dc magnetic field, and depends on the driving field frequency.

II. EXPERIMENTAL

The measurements were carried out at $T = 5$ K on ZrB_{12} single crystal. The sample was grown in the Institute for Problems of Materials Science, Ukraine. Its dimensions are $10.3 \times 3.2 \times 1.2$ mm³ and it was cut by an electric spark from a large crystal of 6 mm diameter and 40 mm length. The surface of the sample was polished mechanically and then chemical etched in boiling $\text{HNO}_3/\text{H}_2\text{O}$ (1:1) for 10 minutes was used. X-ray pictures showed that a sample was single-phase material with the UB_{12} structure (space group $\text{Fm}3\text{m}$, $a = 7.407$ Å [14]. The tunnel characteristics of this sample were described earlier [2]. The dc-magnetic moment was measured using a SQUID magnetometer. A block diagram of the ac linear and nonlinear setup is shown in Fig. 1.

The ac magnetic field $h(t) = h_0 \sin(\omega t)$ was supplied by the magnetometer copper solenoid. The ac response was measured by an inductive pick-up coil method [15]. The sample was put into one coil of a balanced pair of pick-up coils and the induced voltage $V(t) \propto dM(t)/dt$ was measured with an oscilloscope. Here M is the magnetic moment of the sample. The lock-in amplifier was used in order to measure simultaneously in-phase and out-of-phase signals of the first and third harmonics of the driving frequency. An oscilloscope measured the wave

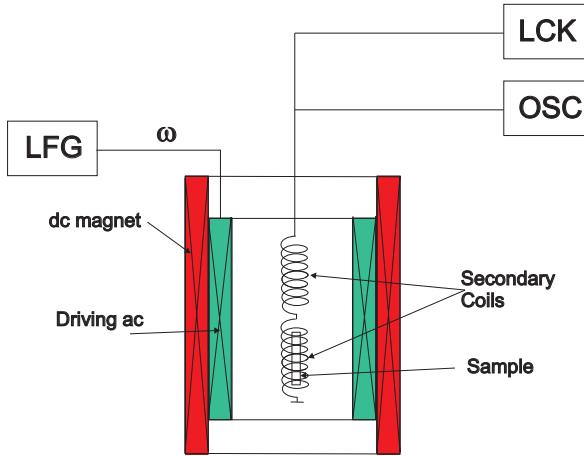


FIG. 1: (Color online) Block diagram of the experimental setup. LFG - low frequency generator, LCK - lock-in amplifier and OSC - oscilloscope.

form of the signal in one channel. The second channel of the oscilloscope measured the time derivative of the excitation field.

III. EXPERIMENTAL RESULTS

Fig. 2a shows the real part of the ac susceptibility at the fundamental frequency, χ' , and the zero-field cooled (ZFC) dc susceptibility, $\chi_{dc} = M/H_0$ as a function of dc field H_0 . The inset to Fig. 2a presents the ZFC magnetization curve at 5 K. Field dependencies of the ac susceptibility imaginary part at fundamental frequency, χ'' , and amplitude of the third harmonic, $A_{3\omega}$ are shown on Fig. 2b and Fig. 2c respectively. Amplitude dependence of the third harmonic, $A_{3\omega}(h_0)$ for $H_0 = 180$ Oe is presented on inset to Fig. 2c. It is clear that this dependence is far to be cubic as the perturbation theory predicts. Experiment shows that amplitude dependence of $A_{3\omega}(h_0)$ is not cubic at any dc field H_0 .

It is clear that the observed large signal of the $A_{3\omega}$ and maximum of the χ'' located in a magnetic field $H_{c2} < H_0 < H_{c3}$, e.g. in a surface superconducting state, although the zero dc signal indicates that bulk of the sample is in the normal state. The absorption in the SSS exceeds losses in the mixed and normal states.

Fig. 3 shows the time derivative of the magnetic moment of a sample at different applied magnetic fields at $T = 5$ K. Note (i) that only in the SSS, the signal does not have the sine-form. (ii) The amplitude dependence of the third harmonic, $A_{3\omega}(h_0)$, presented in the inset to Fig. 2c does not exhibit any cubic dependence.

The experimental data presented in Figs. 2 and 3 are complex and the theoretical model which explains these observations is given in the next section.

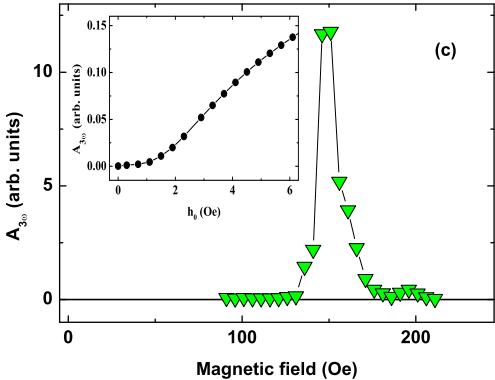
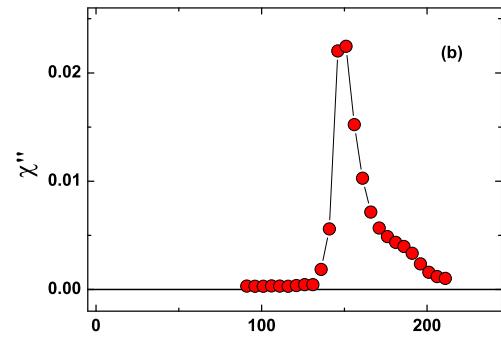
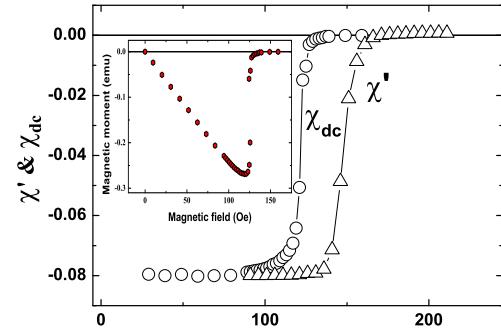


FIG. 2: (Color online) (a) χ' and $\chi_{dc} = M/H_0$ magnetic field dependencies at $T = 5$ K. Inset: magnetization curve after ZFC.

(b) Magnetic field dependence of χ'' .

(c) Field dependence of the amplitude of the third harmonic, $A_{3\omega}$. Inset: amplitude dependence of $A_{3\omega}(h_0)$ at $H_0 = 180$ Oe.

ac measurements were carried out at frequency $\omega/2\pi = 170$ Hz and $h_0 = 0.4$ Oe.

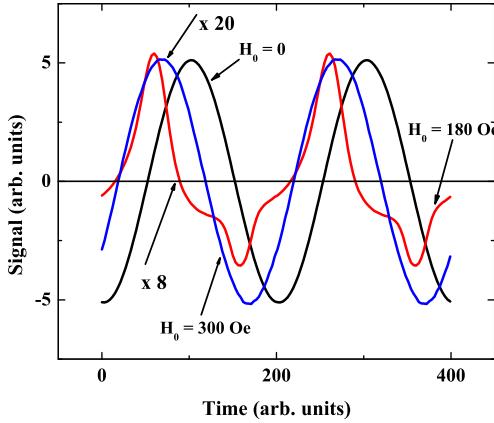


FIG. 3: (Color online) Oscillogram of dM/dt for three different magnetic fields in the Meissner state ($H_0 = 0$), in surface superconducting state, ($H_0 = 180$ Oe $< H_{c3}$), and for a normal state ($H_0 = 300$ Oe $> H_{c3}$) at $h_0 = 4.75$ Oe.

IV. THEORETICAL MODEL

Our theoretical approach is based on the numerical solution of the two Ginzburg-Landau equations [18] for the order parameter and vector potential, which in the normalized form are as follows:

$$\begin{aligned} & -(i\nabla/\kappa + \vec{A})^2\Psi^2 + \Psi - |\Psi|^2\Psi = 0 \\ & -\text{curlcurl}\vec{A} = \vec{A}|\Psi|^2 + i/2\kappa(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*) \end{aligned} \quad (1)$$

The order parameter, Ψ , is normalized with respect to its value in zero magnetic field, the distances with respect to the London penetration length λ , and the vector potential \vec{A} with respect to $\sqrt{2}H_c\lambda$, where H_c is the thermodynamic critical field and $\kappa = \lambda/\xi$ is the Ginzburg-Landau parameter, and ξ is the correlation length. In the second equation for the vector potential we neglected the normal current, assuming that the skin depth exceeds both the London penetration length and sample thickness. It is assumed that the sample form is a slab with $2d$ thickness and that the external magnetic field is parallel to its surface. The chosen coordinates are: the x -axis normal to the slab, (thus the symmetry plane is $x = 0$), and the z -axis is directed along magnetic field. It is assumed that external magnetic field $H > H_{c2} = \kappa$.

Assuming the surface solutions have the form of

$$\Psi(x, y) = f(x)\exp(i\kappa y) \quad (2)$$

therefore, Eqs. 1 reduce to

$$\begin{aligned} & -\frac{1}{\kappa}\frac{\partial^2 f}{\partial x^2} + (A - k)^2 f - f + f^3 = 0 \\ & \frac{\partial^2 A}{\partial x^2} = f^2(A - k), \end{aligned} \quad (3)$$

where k is constant. The boundary conditions at $x = \pm d$ are: $\partial f(\pm d)/\partial x = 0$, $\partial A(\pm d)/\partial x = H$; at $x = 0$ $f(0) = 0$ and $A(0) = 0$; $H = H_0 + h_0\sin(\omega t)$. An additional condition for the surface states $\partial f(0)/\partial x = 0$ is satisfied only asymptotically for $d \rightarrow \infty$. For the equilibrium state the value of $k = k_{eq}$ can be obtained by minimizing the Gibbs free energy defined as:

$$\tilde{F} = \int dV \left\{ \frac{1}{2}|\Psi|^4 - |\Psi|^2 + |i\nabla\Psi/\kappa + A\Psi|^2 + B^2 - 2BH \right\}, \quad (4)$$

where B is the magnetic induction. Using Eq. 3 one then obtains

$$\tilde{F} = -HA(d) - \int_0^d dx \left\{ \frac{1}{2}f^4(x) + A(x)[A(x) - k]f^2(x) \right\} \quad (5)$$

The two coupled Eqs. 3 could be solved by numerical methods. The order parameter for surface solutions deviates from zero only near the sample boundary, and we could consider comparatively small $d/\lambda \leq 10$. The actual sample thickness exceeds λ by 4 or 5 orders of magnitude. The solutions for large d could be found from the ones for small d by transformation $k = k_s + H_i(d - d_s)$, where $H_i = H_s(0, H, K)$ is the magnetic field at $x = 0$ in the problem for $d = d_s \cong 10\lambda$. The index s corresponds to the solution for this small d . This choice of d_s is sufficient for numerical calculations and provides the solutions with $f_s(0) = 0$, $\partial f_s(0)/\partial x = 0$. The free energy transformed as

$$\tilde{F} = \tilde{F}_s - H_i(d - d_s)(H - \int [A_s(x) - k_s]f_s^2(x)dx) \quad (6)$$

To simplify the calculations we use below variable k_s and omit index s . The properties of the equilibrium solutions for a semi-infinite half-space have been discussed in [16]. The order parameter, the supercurrent, and the internal magnetic field were calculated. In these states the total surface current equal zero and free energy reaches a minimum value. The ac magnetic field drives the superconductor into a metastable state. These states correspond to the solutions of Eqs. 3 for $k \neq k_{eq}$. The solution of Eqs. 3 shows that surface states exist in a wide range of k near k_{eq} as shown in the upper panel of Fig. 4, but only for $|k - k_{eq}| \ll k_{eq}$ free energy of these states is lower than the energy of the normal state. Moreover, this range shrinks with increasing sample thickness (Fig. 5).

This is due to the increase of the contribution of the first term in Eq. 5 which is the order of the Gibbs energy of the normal state $\tilde{F}_0 = -H^2d$. The total surface current equals zero for equilibrium k and increases with increasing $|k - k_{eq}|$ as is shown in the lower panel of Fig. 4. For a given k , the free energy versus magnetic field does not exhibit any minimum in the equilibrium. Only the difference between the Gibbs energy of the superconducting and normal states exhibits minimum near equilibrium field as was discussed in [4], but for a such

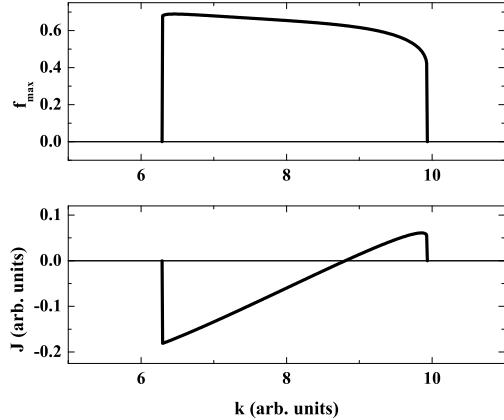


FIG. 4: Upper panel. The maximal value of the order parameter, f_{max} , as a function of k . Lower panel. Total surface current, J , as a function of the k parameter. The equilibrium value of $k = 8.8$ corresponds to zero surface current.

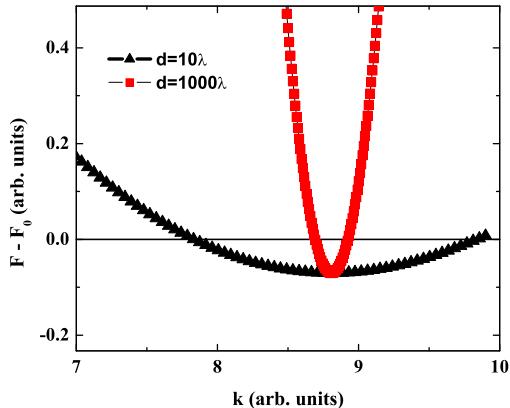


FIG. 5: (Color online) Free energy of the surface superconducting states relative to the free energy of normal state (F_0) in magnetic field $H_0 = 1$ and $k = 0.75$ for two values of the sample thickness.

representation the reference point moved with changing field.

The magnetic moment of the sample actually depends on the total surface current J , because the current is localized in a thin surface layer. This current is a function of the external magnetic field H and k , $J = J(H, k)$. The response of the sample to the ac magnetic field depends on the dynamics of k . A priori, one can assume that the

equation that governs the dynamics is

$$\frac{dk}{dt} = -\nu[k - k_{eq}(H)], \quad (7)$$

where $k_{eq}(H)$ is the equilibrium k in instantaneous value of external magnetic field and $\nu = \nu(k - k_{eq})$ is the relaxation rate. Function $k_{eq}(H)$ has to be found from Eqs. 3 and for $|H - H_0| \ll H_0$ is well approximated by a polynomial of the third order of $h = H - H_0$. Using the function $J(h, k)$ calculated from Eqs. 3 and Eq. 7 one can obtain the time evolution of the surface current in an ac field and compare with observed wave forms. The time derivative of the surface current is proportional to the observed signal V . The coefficient $\alpha = \frac{1}{V} \frac{dJ}{dt}$ depends on the experimental apparatus parameters. Actually we could obtain $k(t)$ directly from experimental data and test the correctness of Eq. 7. We may write

$$\frac{\partial J(h, k)}{\partial h} \frac{dh}{dt} + \frac{\partial J(h, k)}{\partial k} \frac{dk}{dt} = \alpha V(t) \quad (8)$$

This expression permits us to obtain $k(t)$ from the observed wave form. It is a first order differential equation for $k(t)$. To evaluate $k(t)$ we have to know k at $t = 0$ and α , since the derivatives $\partial J / \partial h$ and $\partial J / \partial k$ can be calculated from Eqs. 3. The $k(0)$ value can be found from the condition when the maximal current value during the period is minimal. In order to find α we calculated $J(t)$ assuming that ν in Eq. 7 is constant. Then, we choose the ν value in order to minimize difference between the calculated and experimental data. This procedure gives both ν and α . To be sure that ν is actually constant, one has to collect the weak ac field data. The observed signal during one period of the ac field and the result of a simulation with Eqs. 3 and 7 are shown in Fig. 4. The data in this figure were collected in a dc field of 130 Oe, and an ac field with amplitude 1.78 Oe and frequency $\omega/2\pi = 733$ Hz. In our calculations we took $\nu/\omega = 0.05$ and the Ginzburg-Landau parameter $\kappa = 0.75$ [2]. The good correlation between the calculated and experimental data permits one to find the scale coefficient α which is used below.

V. DISCUSSION

As was shown above the losses are small both in the mixed and normal states and have a maximum at $H_0 > H_{c2}$ (see Fig. 2a). The $H_{c2} = 126$ Oe is determined from the dc magnetization curve (inset to Fig. 2a). The oscillogram, Fig. 3, in both the Meissner and normal states ($H_0 = 0$ and 300 Oe) has a sine shape, and for $H_{c2} < H_0 < H_{c3}$ the wave form deviates from a sine shape. We do not observe any clear plateau for dM/dt in the ac period. Such a plateau is a peculiarity of the Bean model when it is applied to surface currents [4, 17]. Using the experimental data and the model developed

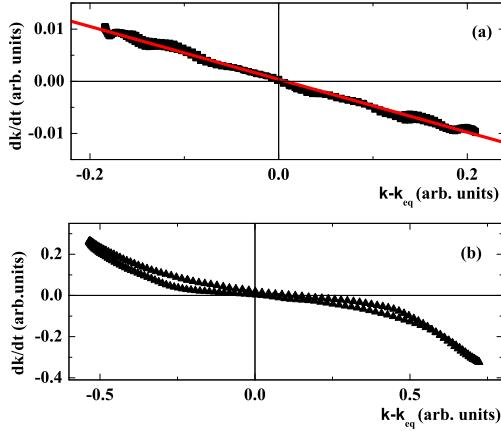


FIG. 6: (Color online) The time derivative dk/dt plotted as a function of $k - k_{eq}$ for at $H_0 = 130$ Oe and $\omega/2\pi = 733$ Hz (a): $h_0 = 1.78$ Oe and (b): $h_0 = 5.9$ Oe. The linear fit of the experimental curve (a) gives $\nu/\omega = 0.051$. The hysteresis at large amplitudes (b) shows that, generally speaking, dk/dt depends on k and the instantaneous magnetic field not only through $k = k_{eq}$.

in previous section one can calculate dk/dt as a function of $k - k_{eq}$. Fig. 6 shows dk/dt plotted as a function of $k - k_{eq}$ obtained from the wave forms that were observed for $H_0 = 130$ Oe and $\omega/2\pi = 733$ Hz. The linear fit of dk/dt at $h_0 = 1.78$ Oe yields $\nu(0)/\omega = 0.051$ which agrees well with the $\nu/\omega = 0.05$ used in Eq. 7 when the scale coefficient has been found. Visible hysteresis in Fig. 6b indicates that at a high amplitude of excitation the relaxation rate in Eq. 7 ν depends on k and on the instantaneous value of $h(t)$ not only through $k - k_{eq}(h)$.

The expression for $\nu(k - k_{eq})$ could be found from fitting of dk/dt by the polynomial of $k - k_{eq}$. The approximation expression which has a form

$$\nu(x)/\omega = 0.051 - 0.117x + 1.323x^2 + 0.184x^3 - 0.747x^4 \quad (9)$$

provides the calculated data, which with an accuracy of better than 10%, reproduces the experimental data for a dc field of 130 Oe and a frequency of 733 Hz as is shown in Fig. 7.

Increasing the dc field leads to the increasing of the relaxation rate ν . We found that for $H_0 = 138$ and 180 Oe, the relaxation parameter for weak ac amplitudes are $\nu(0)/\omega = 0.145$ and 4.725 respectively (see Fig. 8).

The calculated wave forms with the help of the proposed model reproduce experimental data only for a weak ac field as shown in Fig. 9. This is due to the increase in the difference between the two values of dk/dt for the same $k - k_{eq}$ at larger ac amplitudes, (see at Fig. 8b, d).

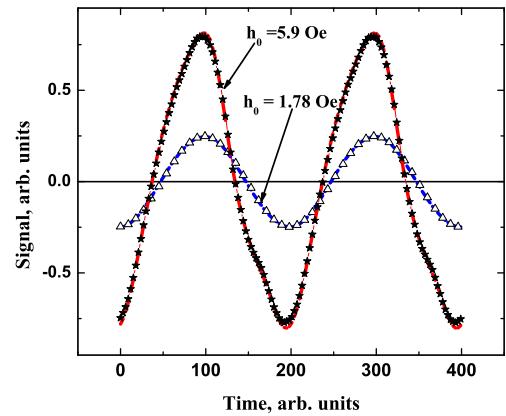


FIG. 7: (Color online) The observed and calculated (solid lines) oscilloscope for $H_0 = 130$ Oe, $\omega/2\pi = 733$ Hz at $h_0 = 1.78$ Oe and $h_0 = 5.9$ Oe.

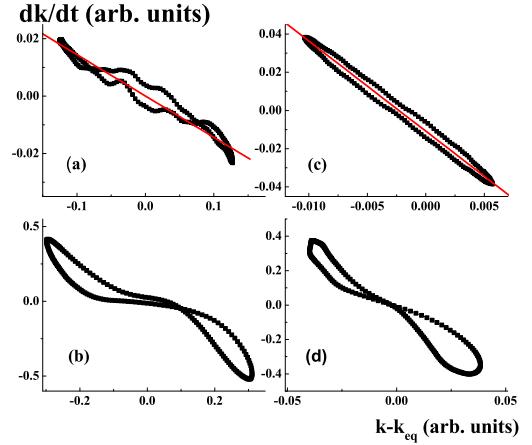


FIG. 8: (Color online) dk/dt as a function of $k - k_{eq}$ at $\omega/2\pi = 733$ Hz. (a) - $H_0 = 138$ Oe, $h_0 = 0.59$ Oe; (b) - $H_0 = 138$ Oe, $h_0 = 5.9$ Oe; (c) - $H_0 = 180$ Oe, $h_0 = 0.59$ Oe; (d) - $H_0 = 180$ Oe, $h_0 = 5.9$ Oe. Linear fit at low amplitude of excitation ((a) and (c) panels) gives $\nu/\omega = 0.144$ for $H_0 = 138$ Oe and $\nu/\omega = 4.73$ for $H_0 = 180$ Oe.

Fig. 10 shows the $dk/dt(k - k_{eq})$ dependence for different frequencies at $H_0 = 130$ Oe and $h_0 = 4.75$ Oe. One may conclude from this figure that the relaxation rate ν (if Eq. 7 could be applied) increases with excitation frequency ω .

It is clear that the model equation 7, where the relaxation rate ν depends on the one variable $k - k_{eq}$, is valid only for small ac amplitudes. The transition from the

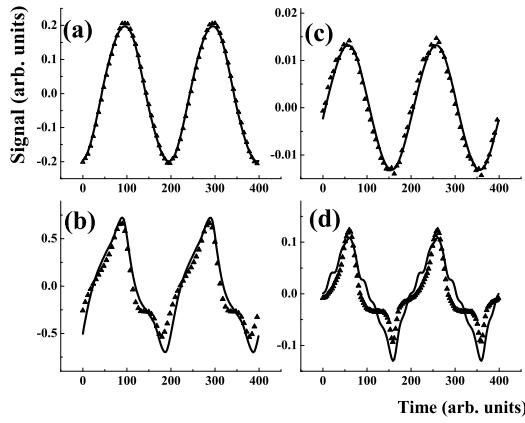


FIG. 9: Calculated (solid lines) and experimental (triangle) oscillograms at $\omega/2\pi = 733$ Hz. (a) - $H_0 = 138$ Oe, $h_0 = 0.59$ Oe; (b) - $H_0 = 138$ Oe, $h_0 = 5.9$ Oe; (c) - $H_0 = 180$ Oe, $h_0 = 0.59$ Oe; (d) - $H_0 = 180$ Oe, $h_0 = 5.9$ Oe.

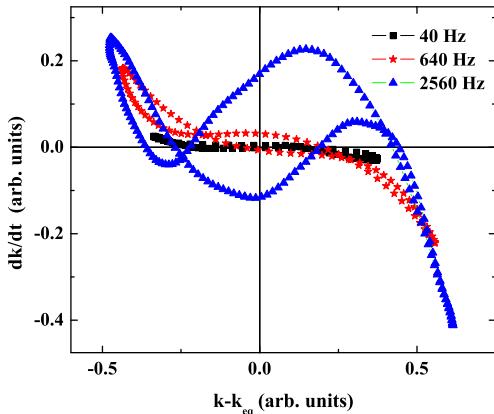


FIG. 10: (Color online) dk/dt as a function of $k - k_{eq}$ at $H_0 = 130$ Oe and $h_0 = 4.75$ Oe for different frequencies.

surface state with one k to another k , requires changing the order parameter in the whole sample. Possibly, it happens through the nucleation of a new phase. This process is governed by excess energy. In general the relaxation constant in Eq. 7 may depend on the energy of the state. Approximately it could be taken into account by the assumption that the relaxation constant depends on $k - k_{eq}$. We see that for small ac fields and not far away from H_{c2} , this assumption is correct. But increasing the

ac amplitude and/or the dc field results in the explicit dependence on both: k and the instantaneous value of

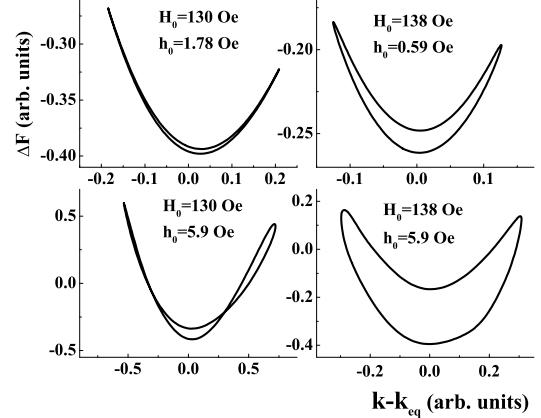


FIG. 11: Calculated dependence of the Gibbs energy as a function of the $k - k_{eq}$ parameter during the ac cycle for different values of the dc field H_0 and amplitude of excitation, h_0 at frequency $\omega/2\pi = 733$ Hz.

the magnetic field H_0 . The straightforward calculations of the Gibbs energy F , exhibited in Fig. 11, shows that when this energy is a single-valued function of $k - k_{eq}$, the simulation with Eq. 7 gives acceptable results.

When F becomes a multivalued function, the calculated wave forms differ from the experimental data. In order to obtain a proper theoretical description, one has to take into account that the energy of SSS is not expressed only through $k - k_{eq}$.

VI. CONCLUSION

We experimentally investigated the dynamics of the surface metastable superconducting states of ZrB_{12} in ac fields at low frequencies (40 - 2500 Hz). It was shown that for low ac amplitudes of excitation these dynamics are governed by a simple relaxation equation. The relaxation rate depends on the deviation from the equilibrium state. Decreasing of the frequency of the applied ac field results in increasing the relaxation time.

VII. ACKNOWLEDGMENTS

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